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BOTANICAL GAZETTE

AUGUST 1896

ON THE TOXIC ACTION OF DISSOLVED SALTS AND THEIR ELECTROLYTIC DISSOCIATION.¹

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THE THEORY OF ELECTROLYTIC DISSOCIATION.

During the last decade work in physical chemistry has been characterized by a thorough and systematic study of solutions from both theoretical and experimental points of view. As a result of the activity along this line our knowledge of the nature of substances dissolved in various solvents has been greatly extended. In 1887 van't Hoff,² basing his argument upon the osmotic experiments performed by Pfeffer³ ten years earlier, was enabled to show almost a complete analogy between the behavior of solutions and gases. This analogy grows out of the fact that when the volume of a solution and its osmotic pressure are taken into consideration the same laws hold as in the case of gases when the volume of the gas and its pressure are considered. So close is the analogy that, considering the temperature constant, the osmotic pressure exerted by a substance dissolved in a certain amount of solvent is the same as the pressure exerted by the gas if the same amount of substance is conceived of as being

¹ Abridged by the authors from a paper soon to appear as a Bulletin of the University of Wisconsin (Science Series).

² Zeitschr. f. physik. Chem. 1: 481.

³ Osmotische Untersuchungen, Leipzig, 1877.

volatilized and as occupying the same volume as that possessed by the solution. Thus van't Hoff showed how the laws of Boyle and Gay-Lussac can be applied to dilute solutions. He was also enabled to make the following important extension of Avogadro's hypothesis: Equal volumes of all solutions having the same temperature and the same osmotic pressure contain an equal number of molecules, which number is identical with that contained in a gas having the same volume, temperature and pressure.

When Avogadro put forth his hypothesis that equal volumes of all gases under the same conditions of temperature and pressure contain an equal number of molecules, facts were found that apparently spoke strongly against this view. Thus it was observed that the vapor density of the chloride of ammonium was only a little more than half as great as was required by the principle of Avogadro, or, in other words, the molecular weight of the chloride of ammonium as calculated from the vapor density was found to be only a little more than one-half of that expressed by the formula NH_4Cl . This fact at first caused much opposition to Avogadro's views, which was finally cleared away, however, when it was shown that in the vapor of the chloride of ammonium there are not simply molecules of that salt, but also hydrochloric acid and ammonia molecules, the products into which ammonium chloride in the vapor state is largely dissociated.

The theory of van't Hoff had to contend with a similar difficulty. While the behavior of many solutions was such as to strongly support the theory, a large number of solutions (particularly aqueous solutions of acids, bases and salts) showed considerable deviation in their behavior from what the theory required, inasmuch as their osmotic pressures were greater than they ought to be according to the theory. The empirical results of Raoult,⁴ which led to the methods for determining molecular weights of dissolved substances from the diminution of the vapor tension (or the elevation of the boiling point) of the

⁴ Compare Ostwald, *Lehrbuch der allgemeinen Chemie* 1:715, 748.

solution or the lowering of the freezing point of the same, were explained from theoretical standpoints by the above mentioned work of van't Hoff, and so these methods were placed upon a thoroughly scientific basis. Solutions that showed too great an osmotic pressure also showed too great a diminution of the vapor tension or too great a lowering of the freezing point, and consequently too small a molecular weight.

In his mathematical formulæ van't Hoff for the time being arbitrarily introduced a factor i to account for the deviations that such solutions showed from what the theory required. Soon, however, Arrhenius,⁵ from the relation between the lowering of the freezing point of solutions and their electrical conductivity, came to the conclusion that in aqueous solutions of salts, acids and bases, in short, in solutions that are conductors of electricity, the dissolved substances showing too small molecular weights (as did the chloride of ammonium in the vapor state) are to be regarded as being dissociated⁶ into part-molecules or ions.⁷ These ions are charged with electricity, each gram-equivalent bearing 96,540 coulombs. This latter figure has been determined by experiments on electrolysis and has well been termed the constant of Faraday's law. There are in a solution of an electrolyte as many ions charged with positive electricity as with negative electricity and thus the electrical neutrality of the solution is preserved.

Viewing things, then, in the light of the theory of Arrhenius, we have, for example, in a solution of sodium chloride sodium ions and chlorine ions, besides a certain number of undissociated sodium chloride molecules. Experiments on the electrical conductivity show that in this case dissociation is practically complete when one gram-molecule (*i. e.*, $23 + 35.5 = 38.5$ grams) of the salt is dissolved in 1000 liters of water. There are at this dilution then in solution not NaCl molecules, but Na ions and Cl ions. These are usually written Na^- and Cl^+ .

⁵ Zeitschr. f. physik. Chem. 1:631. 1887.

⁶ Because this dissociation takes place only in case of electrolysis it is termed electrolytic dissociation.

⁷ A term that dates back to Faraday.

It has often been asked in what way Na ions and Cl ions differ from ordinary sodium in the metallic state and ordinary chlorine gas respectively. The difference lies in the energy possessed by the substances in the ordinary state and in the ionic state. Ten grams of chlorine ions, for example, contain less energy than do ten grams of chlorine. Supply the energy to the ions, as is done in the case of electrolysis, and the ions are changed to ordinary chlorine gas. The lack of understanding of this point at first caused much reluctance to accept the theory of electrolytic dissociation (or the theory of free ions as it is also called), notably on the part of English chemists.

Since Arrhenius published his theory of electrolytic dissociation, all investigations made on salt solutions have confirmed it. In addition to the lowering of the freezing point and the electrical conductivity, the elevation of the boiling point, the specific volume, and the optical and thermal properties of solutions of electrolytes, all strongly support the views of Arrhenius. This theory in the hands of Nernst⁸ has yielded a clearer understanding of the processes that take place in voltaic combinations and has made it possible to calculate with accuracy in advance what the electro-motive force of a galvanic chain will be. It has enabled Ostwald⁹ to place analytical chemistry upon a firmer scientific basis. In short, all the physical and chemical properties of aqueous solutions of electrolytes are well explained by the assumption that in these solutions the dissolved substances are split up into part-molecules or ions, and that the various properties that the solutions possess are due to the properties of the ions.

The more dilute the solution of an electrolyte is, the greater is the percentage of the dissolved substance that is dissociated, and only at infinite dilution is this dissociation complete. In the case of many substances, however, namely strong acids and bases as well as salts of these, dissociation goes on very rapidly

⁸ See Nernst, *Theoretische Chemie* 563-569, where other references will also be found.

⁹ *Die wissenschaftlichen Grundlagen der analytischen Chemie*, Leipzig, 1894.

as dilution increases, so that, as was pointed out above in the case of sodium chloride, dissociation is practically complete when an equivalent in grams is dissolved in 1000 liters of water.

Hydrochloric acid dissociates into H ions and Cl ions. A dilute solution of sodium chloride and one of hydrochloric acid both contain Cl ions. Their difference, then, is due to the fact that the former solution contains H ions, whereas the latter contains Na ions. To this difference are to be ascribed all the differences of properties that the two solutions possess. Solutions of all acids contain H ions, solutions of all chlorides contain Cl ions, those of sulphates SO_4 ions, those of nitrates NO_3 ions. Salts of copper in solution yield Cu ions, those of lead Pb ions, etc. In general, if BA represent the formula of a salt, B representing the basic radical and A the acid radical, then in dilute aqueous solutions this compound is to a greater or less extent dissociated into the ions B^+ and A^- , and, as stated, all the physical and chemical properties that such a solution possesses are due to the properties of the ions together with the properties of the undissociated molecules present.

THE PHYSIOLOGICAL ACTION OF DILUTE SOLUTIONS.

It has always been taken as axiomatic that the physiological action of any substance is due to its chemical character. *Now if, in the case of the solutions in question, all the chemical and physical properties are due to the properties of the ions plus those of the undissociated molecules it contains, it seems very probable that the physiological effect produced by such solutions is also due to these.* This thought, simple as it is, has to our knowledge never before been expressed.

Many investigations on the physiological action of aqueous solutions of salts on bacteria and higher forms of plant life as well as on animals have been made. The strengths of the solutions with which these experiments were performed have always been expressed in per cent. by weight; thus chemically equivalent quantities (*i. e.* molecular quantities) of the different substances were not compared, and it is probably for this reason that general considerations have entirely escaped observation.

If a very dilute solution of sodium chloride differs from a dilute solution of hydrochloric acid only in that the former contains Na ions and the latter H ions, then the poisonous action of the latter is plainly due to the H ions present. In like manner comparing a very dilute solution of sodium nitrate with a similar solution of nitric acid, the poisonous nature of the latter would be due to the H ions present. In general, if the solution is sufficiently dilute so that the acid is completely dissociated and the acid radical is of such a nature that at this concentration its ions have practically no poisonous action, the toxic value of the acid solution is due only to the H ions present. Now strong acids are highly dissociated in aqueous solutions, thus rendering these relatively rich in H ions. Weaker acids are not as strongly dissociated, their solutions contain less H ions, and are consequently less active. It must be borne in mind that the salt remaining undissociated is present in the solution as well as the ions. That these undissociated remainders and the anions of the acid radical also exert an effect is not to be denied, but in many cases, such as that of the Cl ions in hydrochloric acid solutions, the action is practically *nil* at the strength at which hydrochloric acid is still effective, since a solution of common salt containing as many Cl ions as the hydrochloric acid solution in question is ineffective. The same reasoning may be applied to nitrate of sodium and nitric acid, also to sodium hydroxide and common salt. In the latter case the solutions differ from each other in that the former contains OH ions, whereas the latter contains Cl ions. All solutions of bases (lyes) contain OH ions and their toxic action is due to these alone, provided that the metal or radical forming the cation is itself harmless at the concentration used. Thus it is evident that H ions and OH ions have toxic properties. That it is the ionic condition which brings this about is shown by the fact that in the case of water where we have these constituents in practically an undissociated state, there is no toxic action.

The poisonous property of a very dilute solution is then due to the ions it contains, and if at the particular concentration in

hand only one physiologically active ion is present the effectiveness of the solution is to be attributed to that one ion. Solutions of hydrochloric, nitric and sulphuric acids are nearly completely dissociated when an equivalent in grams is dissolved in 1000 liters of water. Hence such or more dilute solutions of these acids, when chemically equivalent quantities are dissolved, ought to have the same toxic effect, the Cl , NO_3 and SO_4 ions at such dilution being harmless. That these radicals are harmless is shown by the fact that like concentrations of the sodium salts of these acids are harmless.

EXPERIMENTAL METHODS.

We have tested this point experimentally for the higher plants by ascertaining the strength of solution in which roots of the ordinary field lupine will just live. We have found that the limit for these acids is reached in case of a solution containing one equivalent in grams in 6400 liters of water. We may say, then, that one gram of hydrogen ions distributed through 6400 liters of water will give a solution in which roots of the lupine will just survive. It is entirely immaterial at this dilution whether we take hydrochloric, nitric or sulphuric acids; the toxic action of the solutions is the same, provided they contain the same amount of hydrogen ions. The molecular weight in grams, or simply one gram-molecule of acid sulphate of potassium in 6400 liters, would contain as much ionic hydrogen as a gram-molecule of hydrochloric acid, and should therefore have the same toxic effect. This has been confirmed by experiment.

It seemed best to confine our first investigations to one order of plants, and, by reason of the nature of the question under consideration, to operate with objects which by previous physiological study have become in a degree well known to botanists. It is for this reason that the seedlings of *Lupinus albus* L. were selected. This seedling is remarkable for its straight, clean radicle, the ease with which uniform specimens can be obtained, and for its great sensitiveness to solu-

tions.¹⁰ The seeds were germinated in the usual manner. After being swelled in water they were placed in moist, loose cotton batting and set in the dark until the radicles had reached a length of from 2^{cm} to 4^{cm}, when they were ready for use.

Experiments were made with solutions contained in glass beakers of convenient size that were, of course, cleaned with the utmost care each time they were used. To support the seedling in proper position the following arrangement was used. Through a large cork fitting loosely over the beaker was thrust a glass rod which played rather tightly through it. Another and smaller piece of cork (small enough to allow ample room about it in the beaker) was likewise tightly pushed on the rod. To the circumference of this inner cork the seedlings were secured by means of glass pins, and by sliding the cork support up or down on the rod they were set into the solution at the desired depth. The large cork, by closing loosely the mouth of the beaker, allowed sufficient change of air within, at the same time preventing undue evaporation from the solution.

Since in the experiments the prime thing sought was the degree of concentration at which each solution just allowed the radicles to live, it became important to avail ourselves of all the means which would aid in deciding whether a radicle was living or dead. As Askenasy¹¹ has pointed out, almost the only reliable indication concerning the condition of a plant is its growth rate. Accordingly access was had to the well known method of Sachs.¹² A fine mark of India ink was made 15^{mm} from the tip of the root, a distance safely including the entire growing zone of the radicle. Thus marked, the roots were placed in the solutions, set in the dark, and again observed after a period of from fifteen to twenty-four hours. In order to deter-

¹⁰ True, On the influence of sudden changes of turgor and of temperature on growth. *Ann. of Bot.* 9:372. 1895.

¹¹ Askenasy, Ueber einige Beziehungen zwischen Wachsthum und Temperatur. *Ber. d. deutsch. bot. Gesellsch.* 8:75. 1890.

¹² Sachs, Ueber das Wachsthum der Haupt- und Nebenwurzeln. *Arb. d. bot. Institut Würzburg* 1:—. 1873, and *Gesammelte Abhandlungen über Pflanzen-physiologie.* 2:778. 1893.

mine the condition of the roots, the general appearance and the growth made after the beginning of the experiment were taken into account. If a much too concentrated solution was used a plainly abnormal aspect was usually found. In the acid solutions the satiny luster of the normal surface was lost and a dead-white color was observed, suggesting a condition perhaps best described by the word *coagulated*. Although difficult to describe, this condition is quickly detected by the observer, and is undubitable evidence of death. An instructive discussion of this and other *post mortem* symptoms has recently been presented by Paul Klemm.¹³ The radicles killed in colored solutions, as salts of copper, iron, cobalt, etc., took on more or less decidedly the color of the medium. Some radicles after death assumed an unusual transparent appearance. This was the case with those in potassium hydroxide, and in mercuric cyanide, potassium ferro and ferricyanide, hydrocyanic acid and potassium cyanide.

Another evidence that death has taken place is seen in the flabby condition following the loss of turgor pressure. This, in the extremely dilute solutions here used, could in no case be due to the osmotic properties of the solutions, and it would be still more improbable that, after fifteen to twenty-four hours in the medium, the flabby appearance could be due to this cause. Turgor accommodation in a normal root, when placed in a solution osmotically equivalent to those here used, would take place very soon,¹⁴ and living roots would be turgid.

Another indication of the condition of the radicles was sought in the changes in length occurring after the beginning of the experiment. In strongly toxic concentrations where death occurred very quickly, the accompanying loss of turgor left the roots shorter than at the beginning of the experiment. As the solutions were increasingly dilute but still, within the time limit of our experiments, fatal, various amounts of growth were found

¹³ Paul Klemm, Desorganisationserscheinungen der Zelle. *Jahrb. f. wiss. Bot.* 28: 30. 1896.

¹⁴ True, *ibid.* 382.

to have taken place before death, sometimes nearly equaling the normal under the prevailing conditions of temperature, etc. It was thus possible from the *ante mortem* growth in a series of solutions to locate roughly the concentration limit sought.

When neither aspect nor growth rate gave plain evidence, the radicles were measured and returned to the solutions to be again observed. If between the last observation and the first, no elongation had occurred, it was inferred that the roots were dead at the time of the former inspection.

Since, as the concentration decreases, an increasingly long exposure is necessary to work fatally, it was decided to choose a period of exposure to the solutions within which the action of the same should be judged. This period was from fifteen to twenty-four hours following the introduction of the roots into the solution. Although the time limit may seem rather broad, it must be borne in mind that solutions were always diluted by one-half, and therefore with a strong time limit, we should still be far from any absolute concentration limit.¹⁵ Individual differences in the seedlings frequently show themselves, one radicle at times being killed, another beside it surviving. In such cases, the first surviving individual indicated the concentration sought.

Usually two seedlings were placed in each concentration tested, but sometimes only one was used. When grounds for doubting the accuracy of results were present, experiments in question were repeated.

It is not to be inferred that the limits here obtained represent the greatest strength of the given substances that these radicles can endure, since a gradual increase of concentration allows a very considerable accommodation on the part of the plant to be made, and the consequent toleration of solutions that would upon immediate use have proved fatal. This was shown in several experiments in which dead roots were left for a time in the solutions. Laterals pushed out above the dead region and grew in the solutions without serious harm.

¹⁵ P. Klemm, *ibid.*, 33 (for acids).

TABULATED DATA.

The detailed results of the most essential experiments are presented in the appended tables. At the top of each table is given its number, the substance used, and, in the second line, the date at which the radicles were set into the solutions, and the date at which the results were observed. The distance at which the mark previously mentioned was placed from the root tip was always 15^{mm}. In the first column appear the concentrations used expressed in gram-molecules or gram-equivalents per liter of the solution. The column headed "length" shows the distance between the line and the root tip, giving, therefore, after subtracting 15^{mm}, the growth made during the period indicated. If further observations and measurements were made, the dates and lengths are placed in adjacent columns. Under "remarks" are verbal indications on the condition of the radicles. Death or survival indicates the condition at the time given in column two. The number of horizontal readings under each concentration shows the number of roots employed and their individual records. For a large majority of the substances, there appears in the table the record of the last plainly fatal dilution and of all weaker solutions as far as tested. Thus the concentration limit in most cases is the second concentration in the table.

It will be noted in the concentrations not fatal, that, in general, the amount of growth increases as the concentration decreases. Since, in these experiments, external conditions were not particularly controlled, the value of the growth rates must not be over-estimated and are significant only in features recurring with regularity.

Tables 1 to 5 show that the seedlings just survive in a solution that contains $\frac{1}{6400}$ gram of hydrogen ions per liter. It is evident from what has been stated before that the anions have no toxic action at this dilution, and that the poisonous action of the solutions is solely due to the hydrogen ions present, inasmuch as these various acids affect the seedlings alike.

1. HYDROCHLORIC ACID (HCl).

(Begun January 9, 8 P.M.; closed January 10, 3 P.M.)

Concentration gm. equiv. per liter	Length	Remarks
$\frac{1}{3200}$	17.8 ^{mm}	flabby, dead
. . .	19.0 "	" "
$\frac{1}{6400}$	29.0 "	appearance normal
. . .	18.5 "	tip dead

2. HYDROBROMIC ACID (HBr).

(Begun January 11, 6 P.M.; closed January 12, 10 A.M.)

Concentration gm. equiv. per liter	Length	Remarks
$\frac{1}{3200}$	18.5 ^{mm}	flabby, dead
. . .	18.0 "	" "
$\frac{1}{6400}$	27.5 "	apparently normal
. . .	23.5 "	flabby, dead
$\frac{1}{12800}$	28.5 "	apparently normal
. . . .	31.5 "	" "

3. NITRIC ACID (HNO₃).

(Begun January 11, 5 P.M.; closed January 12, 10 A.M.)

Concentration gm. equiv. per liter	Length	Remarks
$\frac{1}{3200}$	17.5 ^{mm}	flabby, dead
. . .	17.0 "	" "
$\frac{1}{6400}$	28.0 "	apparently normal
. . .	25.0 "	" "
$\frac{1}{12800}$	30.5 "	" "
. . . .	34.0 "	" "

4. SULFURIC ACID (H₂SO₄).

(Begun January 9, 9 P.M.; closed January 10, 4 P.M.)

Concentration gm. equiv. per liter	Length	Remarks
$\frac{1}{3200}$	19.0 ^{mm}	flabby, dead
. . .	17.5 "	" "
$\frac{1}{6400}$	23.0 "	" "
. . .	27.5 "	apparently normal
$\frac{1}{12800}$	28.0 "	" "
. . . .	27.0 "	" "

5. ACID-POTASSIUM SULFATE (KHSO_4).

(Begun January 10, 6 P.M.; closed January 11, 1 P.M.)

Concentration gm. equiv. per liter	Length	Remarks
$\frac{1}{8200}$	15.5 ^{mm}	flabby, dead
$\frac{1}{6400}$	30.5 "	apparently normal
" "	32.0 "	" "
$\frac{1}{12800}$	24.0 "	" "

6. HYDROCHLORIC ACID. MARCH 7, 10 A.M.

(Concentration : $\frac{1}{8200}$ gm. mol. per liter.)

No.	March 7, 2 P.M. 20° C.		March 7, 8 P.M. 19° C.	
1	18.0 ^{mm}	3.0 ^{mm}	17.6 ^{mm}	flabby
2	18.5 "	3.5 "	19.0 "	"
3	18.5 "	3.5 "	18.5 "	"
4	19.5 "	4.5 "	19.5 "	"
	Av. growth per hr. 0.91 ^{mm}		All dead.	

7. HYDROCHLORIC ACID. MARCH 7, 10 A.M.

(Concentration : $\frac{1}{6400}$ gm. mol. per liter.)

No.	March 7, 2 P.M. 20° C.		March 7, 8 P.M. 19° C.		March 8, 11.30 A.M. 25° C.	
1	19.5 ^{mm}	4.5 ^{mm}	23.0 ^{mm}	3.5 ^{mm}	34.0 ^{mm}	11.0 ^{mm}
2	18.5 "	3.5 "	20.5 "	2.0 "	22.5 "	2.5 "
3	19.5 "	4.5 "	22.0 "	2.5 "	28.0 "	6.0 "
4	19.0 "	4.0 "	22.5 "	3.5 "	34.0 "	11.5 "
	Av. growth per hr. 1.03 ^{mm}		Av. growth per hr. 0.5 ^{mm}		Av. growth per hr. 0.2 ^{mm}	

It will be noticed, on inspecting tables 1 to 5, that in the lowest fatal dilution, a growth prior to death of from 5^{mm} to 10^{mm} usually occurred. This raised the question whether, in case of the acids the hydrogen ions might not act catalytically and hasten the chemical processes of the cells and possibly also the growth of the radicle. Experiments with hydrochloric acid

have thus far yielded entirely negative results. Tables 6 to 11 give the record of these experiments, but more work along this line is needed. The first column simply numbers the experiment; the remainder give the results at the times and temperatures named.

8. DISTILLED WATER (Control). MARCH 7, 10 A.M.

March 7, 2 P.M. 20° C.		March 7, 8 P.M. 19° C.		March 8, 11:30 P.M. 25° C.	
19.0 ^{mm}	4.0 ^{mm}	23.0 ^{mm}	4.0 ^{mm}	31.0 ^{mm}	8.0 ^{mm}
21.5 "	6.5 "	26.5 "	5.0 "	36.5 "	10.0 "
21.0 "	6.0 "	28.5 "	7.5 "	43.0 "	14.5 "
21.0 "	6.0 "	26.0 "	5.0 "	36.0 "	10.0 "
Av. growth per hr. 1.5 ^{mm}		Av. growth per hr. 0.87 ^{mm}		Av. growth per hr. 0.69 ^{mm}	

9. DISTILLED WATER (Control). MARCH 14, 11 A.M.

March 14, 3 P.M. 20° C.		March 15, 10 A.M. 22° C.		March 16, 9:30 A.M. 25° C.		March 17, 11 A.M. 23° C.		March 19, 3 P.M. 20° C.	
18.5 ^{mm}	3.5 ^{mm}	34.5 ^{mm}	16.0 ^{mm}	52.0 ^{mm}	17.5 ^{mm}	66.0 ^{mm}	14.0 ^{mm}	86.5 ^{mm}	20.5 ^{mm}
17.5 "	2.5 "	34.0 "	16.5 "	54.5 "	20.5 "	71.0 "	16.5 "	96.0 "	25.0 "
18.5 "	3.5 "	36.0 "	17.5 "	56.0 "	20.0 "	76.5 "	20.5 "	104.0 "	27.5 "
18.5 "	3.5 "	28.0 "	9.5 "	45.0 "	17.0 "	59.0 "	14.0 "	87.0 "	28.0 "
Av. growth per hr. 0.81 ^{mm}		Av. growth per hr. 0.8 ^{mm}		Av. growth per hr. 0.83 ^{mm}		Av. growth per hr. 0.63 ^{mm}		Av. growth per hr. 0.57 ^{mm}	

10. HYDROCHLORIC ACID. MARCH 14, 11 A.M.

(Concentration : 12800 gm. mol. per liter.)

March 14, 3 P.M. 20° C.		March 15, 10 A.M. 22° C.		March 16, 9:30 A.M. 25° C.		March 17, 11 A.M. 23° C.		March 19, 3 P.M. 20° C.	
17.0 ^{mm}	2.0 ^{mm}	26.0 ^{mm}	9.0 ^{mm}	43.5 ^{mm}	17.5 ^{mm}	65.0 ^{mm}	21.5 ^{mm}	87.5 ^{mm}	22.5 ^{mm}
18.0 "	3.0 "	30.0 "	12.0 "	45.0 "	15.0 "	60.0 "	15.0 "	77.5 "	17.5 "
18.5 "	3.5 "	30.0 "	11.5 "	39.5 "	9.5 "	52.0 "	12.5 "	71.0 "	19.0 "
19.0 "	4.0 "	33.0 "	14.0 "	49.0 "	16.0 "	69.0 "	20.0 "	90.0 "	21.0 "
Av. growth per hr. 0.78 ^{mm}		Av. growth per hr. 0.61 ^{mm}		Av. growth per hr. 0.64 ^{mm}		Av. growth per hr. 0.68 ^{mm}		Av. growth per hr. 0.39 ^{mm}	

II. HYDROCHLORIC ACID. MARCH 14, 11 A.M.

(Concentration : $25\frac{1}{100}$ gm. mol. per liter.)

March 14, 3 P.M. 20° C.	March 15, 10 A.M. 22° C.	March 16, 9:30 A.M. 25° C.	March 17, 11 A.M. 23° C.	March 19, 3 P.M. 20° C.
17.0 ^{mm} 2.0 ^{mm}	29.0 ^{mm} 12.0 ^{mm}	41.0 ^{mm} 12.0 ^{mm}	51.5 ^{mm} 10.5 ^{mm}	72.0 ^{mm} 20.5 ^{mm}
18.5 " 3.5 "	32.0 " 13.5 "	50.0 " 18.0 "	66.0 " 16.0 "	94.5 " 28.5 "
18.5 " 3.5 "	29.0 " 10.5 "	39.0 " 10.0 "	50.0 " 11.0 "	72.0 " 22.0 "
17.5 " 2.5 "	24.0 " 6.5 "	31.5 " 7.5 "	41.0 " 9.5 "	57.0 " 16.0 "
Av. growth per hr. 0.72 ^{mm}	Av. growth per hr. 0.56 ^{mm}	Av. growth per hr. 0.50 ^{mm}	Av. growth per hr. 0.52 ^{mm}	Av. growth per hr. 0.35 ^{mm}

12. POTASSIUM HYDROXIDE (KOH).

(Begun January 9, 9 P.M., closed January 10, 4 P.M.)

Concentration gm. mol. per liter	Length	Remarks
$2\frac{1}{100}$	16.5 ^{mm}	rather transparent—alive(?)
. . .	17.5 "	" " " (?)
$4\frac{1}{100}$	27.0 "	apparently normal—alive
. . .	28.0 "	" " "
$8\frac{1}{100}$	36.0 "	" " "
$16\frac{1}{100}$	32.0 "	" " "
$32\frac{1}{100}$	42.0 "	" " "
$64\frac{1}{100}$	37.5 "	" " "

The above table for potassium hydroxide shows that the seedlings plainly live when the solution contains $\frac{1}{400}$ gm. mol. per liter. The potassium hydroxide used was free from carbon-dioxide at the beginning of the experiment, but of course the solution absorbed the carbon-dioxide given off by the plant as well as some from the air during the progress of the experiment, so that the hydroxyl ion is to be regarded as somewhat more poisonous than the above figures would indicate.

Tables 13 to 15 show that in case of the three copper salts investigated, the strength of the solution in which the seedlings will just survive is $51\frac{1}{100}$ gm. mol. per liter. As these salts can be regarded as practically completely dissociated¹⁶ at this great dilution, and as they act alike, it is evident that this figure gives

¹⁶Compare the tables of the electrical conductivity of copper salts collected by Ostwald in his *Lehrbuch d. allgem. Chem.*, 2:770 [ed. 2]. The electrical conductivity of

the concentration at which the copper ions in the solution are insufficient to kill the beans.

13. COPPER SULFATE (CuSO_4).

(Begun February 26, 4 P.M.; closed February 27, 12 M.)

Concentration gm. mol. per liter	Length	Remarks
$25\frac{1}{6}00$	16.0 ^{mm}	discolored, dead
. . . .	16.5 "	" "
$51\frac{1}{2}00$	21.0 "	alive
. . . .	22.0 "	alive (?), tip slightly discolored
$102\frac{1}{4}00$	32.0 "	alive
$204\frac{1}{8}00$	28.0 "	"

14. COPPER CHLORIDE (CuCl_2).

(Begun February 26, 4 P.M.; closed February 27, 1 P.M.)

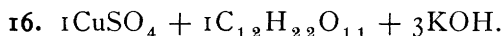
Concentration gm. mol. per liter	Length	Remarks
$25\frac{1}{6}00$	16.2 ^{mm}	dead
. . . .	17.0 "	"
$51\frac{1}{2}00$	19.0 "	alive (?), tip slightly darkened
. . . .	18.0 "	alive
$102\frac{1}{4}00$	21.0 "	"
$204\frac{1}{8}00$	26.5 "	"

15. COPPER ACETATE. $-\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2$.

(Begun February 26, 5 P.M.; closed February 27, 12 M.)

Concentration gm. mol. per liter	Length	Remarks
$25\frac{1}{6}00$	16.0 ^{mm}	dead
. . . .	16.0 "	"
$51\frac{1}{2}00$	23.0 "	alive
. . . .	22.0 "	"
$102\frac{1}{4}00$	21.0 "	"
. . . .	21.0 "	"
$204\frac{1}{8}00$	28.0 "	"
. . . .	26.0 "	"

solutions of the compounds used in the above tables 1 to 6, as well as of most of the inorganic substances mentioned in this paper, are also to be found in Ostwald's Lehrbuch, 2:722-772.

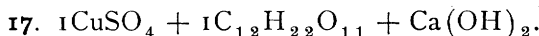


200 cc. CuSO_4 , $\frac{1}{200}$ gm. mol. per liter; 200 cc. sugar, $\frac{1}{100}$ gm. mol. per liter;
3 cc. normal KOH.

(Begun December 5, 8 P.M.)

Concentration gm. mol. per liter	Length Dec. 6, 9 A.M.	Length Dec. 9, 9 A.M.	Remarks
$\frac{1}{400}$...	18.0 ^{mm} 19.0 "	22.0 ^{mm} 21.0 "	living "

(Slight precipitate, probably due to contact with air and CO_2 excreted from roots.
Concentration given based on CuSO_4 content.)



200 cc. CuSO_4 , $\frac{1}{200}$ gm. mol. per liter; 400 cc. sugar, $\frac{1}{100}$ gm. mol. per liter;
106.4 cc. $\text{Ca}(\text{OH})_2$ (saturated solution).

(Begun December 5, 8 P.M.)

Concentration gm. mol. per liter.	Length Dec. 6, 9 A.M.	Length Dec. 9, 9 A.M.	Remarks
0.00142	19.5 ^{mm} 19.5 " 18.5 "	46.0 ^{mm} 48.5 " 46.5 "	alive " "

(Solution deep blue. A slight precipitate formed on standing. Concentration
given based on CuSO_4 content.)

It has been shown¹⁷ recently that in Fehling's solution and allied solutions containing copper the copper does not exist as an ion by itself, but as a part of a complex ion formed with the organic substance present. Such complex ions, according to our theory, we should naturally expect to have a quite different toxic action from that shown by copper ions. Experiment has verified this. In tables 16 and 17 are given the results obtained with solutions of the character just mentioned. The composition of the solution is indicated in each table. Cane sugar was used instead of Rochelle salts in order to avoid getting too many salts into the solution. An excess of caustic alkali was also avoided for it would have introduced hydroxyl ions into the solution which are of themselves poisonous. The beans grow in this

¹⁷ Kahlenberg, Zeitschr. f. physik. Chem. 8: 587, 608-613.

case in solutions that are perfectly blue in color and contain $\frac{1}{400}$ gram atom copper per liter. The enormous contrast that this result presents with that obtained in the experiments in which the copper exists in the solution as ion (tables 14 and 15) is apparent and shows that the copper ion is far more poisonous than the complex ion which contains copper.

18. FERRIC CHLORIDE (FeCl_3).

(Begun December 5, 9 P.M.)

Concentration gm. per liter	Length Dec. 6, 9 A.M.	Length Dec. 9, 9 A.M.	Remarks
Fe, 0.0477 } Cl, 0.0906 }	15.0 ^{mm}		dead, mahogany red
	15.7 "		" " "
Fe, 0.00500 } Cl, 0.00930 }	19.7 "		turgor gone, dead
	20.5 "		" " "
Fe, 0.00250 } Cl, 0.00477 }	21.5 "	21.0 ^{mm}	dead
	21.5 "	21.5 "	"

(Concentration allowing growth not reached. Probably found at next dilution with half the Fe and Cl content of the last in the table.)

19. DIALYZED IRON (FeCl_3).

(Begun November 21, 5 P.M.)

Concentration	Length Nov. 22, 9 A.M.	Length Dec. 2, 9 A.M.	Remarks
Fe, 0.009555% } Cl, 0.0093 }	18.5 ^{mm}		dead, laterals form in solution
	17.5 "		" " " " "
Fe, 0.00477% } Cl, 0.00047 }	23.5 "	51.5 ^{mm}	living, surface reddish
	24.0 "	62.0 "	" " "
	26.0 "	51.5 "	" " "

From table 18, giving the results obtained with ferric chloride, it is evident that ferric ions have a quite strong toxic action. It is known that ferric chloride splits up hydrolytically in dilute solutions, which makes this case somewhat complicated. The main object, however, was to compare the action of the ferric

chloride solution with that of a solution of dialyzed iron,¹⁸ which contains no ferric ions inasmuch as potassium ferrocyanide (which is a test for ferric ions) produces no precipitate in the solution. The absence of chlorine ions in the solution is shown by the fact that silver nitrate produces no turbidity in such a solution. The tables show conclusively that ferric ions are much more poisonous than are the complex ions containing ferric iron in the dialyzed iron solution.

20. FERROUS SULFATE (FeSO_4).

(Begun March 7, 12 M.; closed March 8, 12 M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{12800}$	18.0 ^{mm}	dead, purplish spotted
.....	19.0 "	" " "
$\frac{1}{25600}$	24.0 "	alive, tip somewhat discolored
.....	22.0 "	dead, discolored
$\frac{1}{51200}$	34.0 "	alive, root-tip dead
.....	29.0 "	" " "

Table 20 shows that for ferrous ions the concentration limit at which the seedlings will just survive is $\frac{1}{51200}$ gram ion per liter. The same limit obtains in case of the nickel and cobalt ions (tables 21 to 24). Two nickel salts and also two cobalt salts were tested in order to show again that it is immaterial at this dilution whether the nitrates or the sulphates are used; in other words, that the toxic action of the solutions is solely due to the ions of the metals present.

21. NICKEL SULFATE (NiSO_4).

(Begun March 7, 11 A.M.; closed March 8, 12 M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{2560}$	19.0 ^{mm}	dead
..	22.0 "	"
$\frac{1}{51200}$	33.5 "	alive
.....	31.0 "	"

¹⁸The solution of dialyzed iron used in the experiments of table 19 was prepared according to the directions given in the British pharmacopœia.

22. NICKELOUS NITRATE ($\text{Ni}(\text{NO}_3)_2$).

(Begun March 20, 4 P.M.)

Concentration gm. mol. per liter	Length March 21, 10 A.M.	Length March 23, 3 P.M.	Remarks
$25\frac{1}{6}00$	26.0 ^{mm}	26.5 ^{mm}	dead
. . . .	20.0 "	20.0 "	"
$51\frac{1}{2}00$	28.0 "	28.0 "	"
. . . .	37.0 "	45.0 "	" liv. Mar. 21

23. COBALTOUS SULFATE (CoSO_4).

(Begun March 20, 3 P.M.)

Concentration gm. mol. per liter	Length March 21, 10 A.M.	Length March 23, 3 P.M.	Remarks
$12\frac{1}{8}00$	20.0 ^{mm}	19.0 ^{mm}	dead
. . . .	22.0 "	22.0 "	"
$25\frac{1}{6}00$	23.0 "	27.5 "	" liv. Mar. 21
. . . .	27.0 "	33.0 "	" " " "
$51\frac{1}{2}00$	35.0 "	61.5 "	alive
. . . .	35.0 "	46.0 "	dead, liv. Mar. 21

24. COBALTOUS NITRATE ($\text{Co}(\text{NO}_3)_2$).

(Begun November 23, 5 P.M.; closed March 24, 3 P.M.)

Concentration gm. mol. per liter	Length	Remarks
$25\frac{1}{6}00$	38.0 ^{mm}	alive
. . . .	15.5 "	dead
$51\frac{1}{2}00$	40.0 "	alive
. . . .	28.0 "	"

That cobalt, nickel and iron in the ionic condition thus have the same toxic effect would tend to arouse in the mind of the chemist the question whether this is not connected with the fact that these metals have nearly the same atomic weight. Whether there is a definite relation between the toxic effects of the ions of the metals and the atomic weights of the latter, in other words whether the periodic law finds application here, is a question that can be answered only after more experimental data have been gathered.

25. CADMIUM NITRATE ($\text{Cd}(\text{NO}_3)_2$).

(Begun March 23, 5 P.M.)

Concentration gm. mol. per liter	Length March 24, 3 P.M.	Length March 25, 3 P.M.	Remarks
$\frac{1}{102400}$	20.0 ^{mm}	19.5 ^{mm}	dead
...	21.0 "	20.5 "	"
$\frac{1}{204800}$	29.0 "		alive
...	24.0 "		"

This table shows that cadmium ions are exceedingly poisonous in character.

26. POTASSIUM CYANIDE (KCN)

(Begun February 3, 4 P.M.; closed February 4, 4 P.M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{6400}$	17.5 ^{mm}	alive, near boundary
...	18.0 "	" " "
$\frac{1}{12800}$	20.5 "	"
...	21.0 "	"
$\frac{1}{25600}$	25.0 "	"
...	18.0 "	"
$\frac{1}{51200}$	30.0 "	"
$\frac{1}{102400}$	26.5 "	"
$\frac{1}{204800}$	33.5 "	"

27. POTASSIUM FERROCYANIDE (K_4FeCn_6).

(Begun December 15, 7 P.M.)

Concentration gm. mol. per liter	Length Dec. 14, 12 M.	Length Dec. 17, 9 A.M.	Remarks
$\frac{1}{100}$	17.0 ^{mm}		dead, transparent
$\frac{1}{200}$	17.0 "	21.5 ^{mm}	living, appearance normal
...	16.0 "	17.5 "	" " "
$\frac{1}{400}$	19.5 "	19.0 "	dead
...	17.5 "	18.0 "	living, ap. nor.
$\frac{1}{800}$	20.0 "	21.5 "	" " "
...	20.5 "	23.5 "	" " "
$\frac{1}{1600}$	24.5 "	30.0 "	" " "
...	24.5 "	33.5 "	" " "

28. POTASSIUM FERRICYANIDE (K_3FeCn_6).

(Begun December 13, 8 P.M.)

Concentration gm. mol. per liter	Length Dec. 14, 1 P.M.	Length Dec. 17, 10 A.M.	Remarks
$\frac{1}{200}$	18.5 ^{mm}	18.5 ^{mm}	alive, boundary
...	19.0 "	19.0 "	" "
$\frac{1}{400}$	20.5 "	26.0 "	" "
...	20.0 "	20.0 "	" "
$\frac{1}{800}$	27.5 "	41.0 "	" "
...	25.0 "	37.0 "	" "
$\frac{1}{1600}$	27.5 "	52.0 "	" "
...	25.5 "	45.0 "	" "

Table 26 gives the concentration of cyanogen ions that the lupines can bear; it is about the same as that for hydrogen ions. In potassium ferrocyanide and potassium ferricyanide the iron and the cyanogen radical form complex ions¹⁹ which, as tables 27 and 28 show, have the same toxic effect. This is much less, however, than in the case where iron exists in the solution as an ion by itself or where cyanogen ions as such are present in the solution.

Experiments were also performed with a solution of mercuric chloride. The detailed results of these have unfortunately been mislaid, but the concentration of this solution that the lupines can bear was found to be $\frac{1}{12800}$ gm. equivalent per liter. Mercuric chloride is a compound that is but slightly dissociated at concentrations at which it is ordinarily used in laboratories; at the above mentioned concentration, however, the dissociation must have advanced to a considerable degree.

From a solution of mercuric chloride mercuric oxide can be precipitated by means of potassium hydroxide. If, however, a considerable amount of dextrine be first added to the mercuric chloride solution caustic alkali no longer precipitates mercuric oxide. The solution remains clear, which shows that mercuric ions no longer are present and that the mercury has united with the dextrine to form a complex ion. The latter ions are not as poisonous as mercuric ions, as is apparent from table 29.

¹⁹ These ions are $Fe''CN_6$ and $Fe'''CN_6$ respectively.

29. MERCURIC CHLORIDE + DEXTRINE + CAUSTIC POTASH.

The detailed record having been mislaid, the end results are here given.

(Concentrations calculated on the mercuric chloride.)

Concentration gm. mol. per liter	Result
$\frac{1}{200}$	died
$\frac{1}{400}$	"
$\frac{1}{800}$	"
$\frac{1}{1600}$	"
$\frac{1}{3200}$	"
$\frac{1}{6400}$	lived
$\frac{1}{12800}$	"

30. MERCURIC CYANIDE (HgCN_2).

(Begun February 25, 5 P.M.; closed February 26, 3 P.M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{25600}$	24.0 ^{mm}	transparent in growing parts, dead
.....	28.5 "	" " " "
$\frac{1}{51200}$	28.5 "	dead
.....	30.0 "	"
$\frac{1}{102400}$	45.0 "	alive
$\frac{1}{104800}$	44.0 "	"
$\frac{1}{409600}$	45.0 "	"
$\frac{1}{819200}$	44.0 "	"
.....	46.0 "	"

Mercuric cyanide solutions possess no measurable electrical conductivity. This compound is then practically not dissociated in its solutions. Its toxic effect is consequently due to the undissociated salt (HgCN_2) in the solution. The fact that the roots can bear only $\frac{1}{102400}$ gm. mol. per liter of this substance speaks for its pronounced poisonous character.

In tables 31 and 32 are the results obtained with solutions of silver nitrate and silver sulfate respectively. That these solutions behave alike toward the lupines is again evidence that it is only the silver ions they contain that are active. Their extremely poisonous character will be noted. They are the most poisonous ions that we have investigated.

31. SILVER NITRATE (AgNO_3).

(Begun February 3, 6 P.M.; closed February 4, 10 A.M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{204800}$	17.5 ^{mm}	dead
$\frac{1}{409600}$	20.0 "	alive (?)
$\frac{1}{819200}$	22.0 "	alive
.....	17.0 "	"
$\frac{1}{1638400}$	22.0 "	"

32. SILVER SULFATE (Ag_2SO_4).

(Begun March 23, 5 P.M.)

Concentration gm. equiv. per liter	Length March 24, 3 P.M.	Length March 25, 3 P.M.	Remarks
$\frac{1}{204800}$	21.0 ^{mm}		discolored, dead
.....	16.0 "		" "
$\frac{1}{409600}$	23.0 "	22.0 ^{mm}	dead
.....	25.0 "	26.0 "	" (?)
$\frac{1}{819200}$	25.0 "		alive, distorted
.....	29.0 "		" "

33. SILVER NITRATE (AgNO_3) $\frac{1}{10}$ gm. mol. per liter, 10cc.POTASSIUM CYANIDE (KCN) $\frac{1}{10}$ " " " " 30cc.

(Concentrations estimated on basis of Ag present.)

(Begun April 14, 4 P.M.)

Concentration gm. mol. per liter	Length April 15, 4 P.M.	Length April 17, 4 P.M.	Remarks
$\frac{1}{6400}$	22.0 ^{mm}	22.0 ^{mm}	dead, discolored
.....	21.0 "	22.0 "	" "
$\frac{1}{12800}$	22.0 "	23.0 "	" "
.....	21.0 "	22.0 "	" "
$\frac{1}{25600}$	20.0 "	20.0 "	" "
.....	24.0 "	26.5 "	alive April 15
$\frac{1}{51200}$	25.0 "	27.0 "	" "
.....	26.0 "	31.0 "	" "
$\frac{1}{102400}$	26.5 "	33.5 "	living
.....	29.5 "	39.0 "	"
$\frac{1}{204800}$	32.0 "	41.5 "	"
.....	31.0 "	51.5 "	"
$\frac{1}{409600}$	35.0 "	61.0 "	"

34. SILVER NITRATE (AgNO_3) $\frac{1}{10}$ gm. mol. per liter, 10cc.
 POTASSIUM CYANIDE (KCN) $\frac{1}{10}$ " " " " 27.5cc.
 (Concentrations based on Ag present.)
 (Begun April 14, 5 P.M.)

Concentration gm. mol. per liter	Length April 15, 4 P.M.	Length April 17, 4 P.M.	Remarks
$\frac{1}{12800}$	21.0 ^{mm}	21.0 ^{mm}	dead
. . . .	20.0 "	20.0 "	"
$\frac{1}{25600}$	20.0 "	21.5 "	" alive Apr. 15
. . . .	24.0 "	26.0 "	" " "
$\frac{1}{51200}$	22.5 "	25.0 "	living
. . . .	24.5 "	26.0 "	"
$\frac{1}{102400}$	24.0 "	36.5 "	"
. . . .	23.5 "	27.0 "	"
$\frac{1}{204800}$	31.0 "	46.0 "	"
. . . .	31.0 "	30.0 "	dead
$\frac{1}{409600}$	31.0 "	55.0 "	living

When silver nitrate in solution is treated with potassium cyanide solution, a precipitate of silver cyanide is formed, which upon further addition of potassium cyanide redissolves. The solution of silver cyanide in cyanide of potassium is due to the formation of potassium silver cyanide, KAgCN_2 , which in aqueous solutions dissociates into the ions K^+ and AgCN_2^- . The latter are very stable, and we should naturally expect from the theory that they have a different toxic action from the Ag ions. This is confirmed by experiment. The results are given in tables 33 and 34 which show that the ions AgCN_2^- are far less poisonous than silver ions.²⁰

A few other inorganic acids will now be considered, the action of which is not quite as readily explained as that of the acids mentioned in tables 1 to 4. Hydrocyanic acid is practically not dissociated in aqueous solutions, for its electrical conductivity is almost *nil*. The toxic action of this acid must be due, then, to the undissociated HCN present in the solution. Table 35 shows that the lupines will bear $\frac{1}{12800}$ gm. mol. per liter of this acid.

²⁰ Compare iron and the potassium ferro- and ferricyanides as given above.

Although phosphoric acid is a tribasic acid, the electrical conductivity of its solution shows that it splits up chiefly into the ions H^+ and $H_2PO_4^-$,²¹ and consequently we should expect

²¹ See Ostwald's *Lehrbuch*, *loc. cit.*

a solution containing phosphoric acid (made up molecularly) to show the same concentration at which the plants will grow in it as a solution of hydrochloric acid for instance, for the content of hydrogen ions is the same in both cases. Experiment verifies this as table 35 shows.

35. HYDROCYANIC ACID (HCN).

(Begun March 2, 4 P.M.)

Concentration gm. mol. per liter	Length March 3, 5 P.M.	Length March 4, 3 P.M.	Remarks
$\frac{1}{6400}$	17.0 ^{mm}		dead
.....	16.5 "		"
$\frac{1}{12800}$	17.0 "	17.0 ^{mm}	"
.....	21.5 "	25.5 "	alive
$\frac{1}{25600}$	21.5 "		"
.....	21.0 "		"
$\frac{1}{51200}$	23.5 "		"
.....	39.5 "		"

36. PHOSPHORIC ACID (H_3PO_4).

(Begun January 31, 4 P.M.; closed February 1, 1 P.M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{3200}$	17.0 ^{mm}	flabby, dead
.....	19.5 "	" "
$\frac{1}{6400}$	33.5 "	apparently normal
.....	28.5 "	" "
$\frac{1}{12800}$	27.0 "	" "
.....	21.0 "	" "

Table 36 shows the toxic effect of a solution of chromic acid. This is a weak acid and is probably not completely dissociated at the concentration at which the roots survive in it. Whether the ion $-Cr_2O_7^-$ is harmless at this concentration can of course only

be settled by testing a solution of potassium bichromate or sodium bichromate, in which cases the salts are to a high degree dissociated. The cations are harmless, and consequently the concentration limit for the ion Cr_2O_7 can be found.

37. CHROMIC ACID ($\text{H}_2\text{Cr}_2\text{O}_7$).²²

(Begun February 1, 5 P.M.)

Concentration gm. mol. per liter	Length February 2, 3 P.M.	Length February 3, 11 A.M.	Remarks
$\frac{1}{3200}$	17.0 ^{mm}		dead
....	17.5 "		"
$\frac{1}{6400}$	22.0 "	27.0 ^{mm}	alive
....	28.0 "	34.5 "	"
$\frac{1}{12800}$	25.0 "		"
....	18.0 "		"

38. BORIC ACID.

(Begun February 3, 1 P.M.; closed February 4, 10 A.M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{2}{25}$	18.0 ^{mm}	dead
..	16.0 "	"
$\frac{1}{25}$	16.5 "	"
..	18.0 "	alive (?)
$\frac{1}{50}$	17.5 "	living (?)
..	21.5 "	"
$\frac{1}{100}$	28.5 "	apparently normal
..	28.0 "	" "
$\frac{1}{200}$	39.0 "	" "
....	35.0 "	" "
$\frac{1}{400}$	32.0 "	" "
$\frac{1}{800}$	29.5 "	" "
....	41.5 "	" "
$\frac{1}{1600}$	29.5 "	" "
....	22.5 "	" "
$\frac{1}{3200}$	28.0 "	" "
....	35.0 "	" "
$\frac{1}{6400}$	30.5 "	" "
....	39.5 "	" "

Boric acid solutions are poor conductors of electricity. The acid is then but very slightly dissociated. Experiments on this acid seemed desirable since it is used so much as an antiseptic.

²² See Ostwald, Zeitschr. f. physik. Chem. 2:78.

39. MANNITE.

(Begun February 3, 1 P.M.; closed February 4, 10 A.M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{2}{25}$	26.5 ^{mm}	alive
..	34.5 "	"
$\frac{1}{25}$	32.5 "	"
..	31.5 "	"
$\frac{1}{50}$	27.0 "	"
$\frac{1}{100}$	26.0 "	"
$\frac{1}{200}$	44.0 "	"
$\frac{1}{400}$	37.0 "	"

40. BORO-MANNITIC ACID.

(Begun February 3, 1 P.M.; closed February 4, 10 A.M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{25}$	15.5 ^{mm}	dead
..	16.5 "	"
$\frac{1}{50}$	18.5 "	" (?)
..	18.0 "	" (?)
$\frac{1}{100}$	22.0 "	alive
$\frac{1}{200}$	32.0 "	"
$\frac{1}{400}$	34.0 "	"
$\frac{1}{800}$	35.0 "	"
$\frac{1}{1600}$	34.0 "	"

41. BORIC ACID AND CANE SUGAR.

(Begun February 3, 5 P.M.; closed February 4, 10 A.M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{25}$	16.5 ^{mm}	alive ?
..	17.0 "	" !
$\frac{1}{50}$	19.0 "	" !
..	19.0 "	" !
$\frac{1}{100}$	22.5 "	"
...	20.0 "	"

Table 38 shows the results that were obtained. From these the weak action of the acid is apparent. Mannite has no toxic action on the seedlings, as is shown by table 39; however, it is well known that when boric acid and mannite solutions are

mixed the resulting solution has an acid reaction caused by the presence of hydrogen ions that have resulted from the electrolytic dissociation of a complex boro-mannitic acid that has been formed in the solution. We should, therefore, expect such a solution of boric acid mannite, containing more hydrogen ions than a solution which contains the same amount of boric acid but without the mannite, to have a greater toxic effect than the latter. Table 40 shows results that confirm this. Cane sugar and boric acid do not form a complex acid with each other, consequently no increase of concentration of hydrogen ions is caused by mixing them, and of course we should expect the mixture to have the same toxic action as an equivalent solution of boric acid without addition of cane sugar. A comparison of tables 38 and 41 shows that this is in accord with experimental facts.

In his extensive work on the affinity of constants of organic acids, Ostwald²³ determined the electrical conductivity of a large number of acids, thus giving us a knowledge of the degree to which these acids are dissociated in their solutions. The most dilute solutions with which he worked contained 1 gm equivalent in 1024 liters. Only a relatively small number of the acids he investigated are highly dissociated at this concentration. In investigating the toxic effect of organic acids upon the lupines, it was found that the concentrations in which the plants would just survive are less than 1 gm. equivalent in 1024 liters, so that it is impossible from Ostwald's determinations to tell to what degree the acids are dissociated at these higher dilutions. In only a few of the cases investigated can the acid be considered as practically completely dissociated, as was done in case of the strong mineral acids, so that the effect of the undissociated acid present cannot be left out of account. This anion, too, in many cases no doubt exerts a distinct poisonous action of its own.

Typical acids from the fatty series and from the aromatic series were investigated. The results are given in the tables that follow.

²³ Zeitschr. f. physik. Chem. 3:170, 241, 369.

42. FORMIC ACID.

(Begun January 11, 8 P.M.; closed January 12, 11 A.M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{3200}$	21.5 ^{mm}	flabby, dead
...	19.0 "	" "
$\frac{1}{6400}$	28.0 "	apparently normal
...	27.5 "	" "
$\frac{1}{12800}$	34.0 "	" "
...	26.0 "	" "

43. ACETIC ACID.*

(Begun January 11, 9 P.M.; closed January 12, 11 A.M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{3200}$	18.5 ^{mm}	dead
...	18.0 "	"
$\frac{1}{1600}$	25.0 "	alive
$\frac{1}{3200}$	31.5 "	"
$\frac{1}{6400}$	30.5 "	"
$\frac{1}{12800}$	30.0 "	"

44. PROPIONIC ACID.†

(Begun January 11, 10 P.M.; closed January 12, 11 A.M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{1600}$	18.5 ^{mm}	dead
$\frac{1}{3200}$	28.5 "	alive
$\frac{1}{6400}$	28.0 "	"
$\frac{1}{12800}$	34.0 "	"

45. BUTYRIC ACID.

(Begun January 14, 10 P.M.)

Concentration gm. mol. per liter	Length Jan'y 15, 10 A.M.	Length Jan'y 15, 6 P.M.	Remarks
$\frac{1}{800}$	18.0 ^{mm}	18.0 ^{mm}	dead
...	18.0 "		
$\frac{1}{1600}$	18.5 "	18.5 "	dead
...	18.5 "	18.5 "	"
$\frac{1}{3200}$	20.0 "	23.0 "	alive

* Repeated with same boundary.

† Repeated with same result.

46. VALERIANIC ACID.

(Begun January 15, 4 P.M.; closed January 16, 3 P.M.)

Concentration gm. mol. per liter	Length	Remarks
$1\frac{1}{6000}$	19.0 ^{mm}	dead
. . .	16.0 "	"
$3\frac{1}{2000}$	28.0 "	alive
. . .	28.5 "	"

From table 42 it appears that the lupines survive in a solution of formic acid containing $\frac{1}{6400}$ gm. mol. per liter, the same concentration as in the case of the strong mineral acids. According to Ostwald's determination, formic acid is dissociated to the extent of 35.85 per cent. when one gm. mol. is present in 1024 liters. At 6400 it would be much more highly dissociated. From the result it would appear that dissociation is nearly complete at this high dilution, for the critical concentration is that obtained in case of the strong mineral acids. Whether this is true or not can be better decided after the effect of sodium formate on the seedlings has been studied. Table 43 shows that the radicles can bear much more acetic acid than formic. Acetic acid is not as strongly dissociated. Propionic, butyric and valerianic acids (tables 44 to 46) show the same critical concentration, $3\frac{1}{2000}$ gm. mol. per liter. Ostwald's measurements show that these acids at 1024 are dissociated to approximately the same degree; and, as they are closely allied chemically, one would expect them to have the same effect on the roots. The content of hydrogen ions of the solutions is nearly the same, and the undissociated parts together with the anions would have about the same effect. Acetic acid is a little more strongly dissociated than the last named acids; the fact that nevertheless the seedlings will bear a greater concentration shows that it is not merely the contact of hydrogen ions that comes into consideration here, but that the action of the undissociated acid and the anions makes itself felt.

Glycollic acid is somewhat more strongly dissociated than

lactic acid, so a greater toxic effect would be expected from the former than from the latter considering only the concentration of the hydrogen ions. A comparison of tables 47 and 48 shows that glycollic acid does have a greater poisonous action.

47. GLYCOLLIC ACID.

(Begun January 28, 5 P.M.; closed January 29, 9 A.M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{8200}$	19.0 ^{mm}	dead
. . .	19.5 "	"
$\frac{1}{6400}$	22.0 "	alive
. . .	27.5 "	"

48. LACTIC ACID.

(Begun January 28, 6 P.M.)

Concentration gm. mol. per liter	Length Jan'y 29, 9 A.M.	Length Jan'y 31, 4 P.M.	Remarks
$\frac{1}{1600}$	18.0 ^{mm}	35.0 ^{mm}	flabby, dead
. . .	17.0 "		" "
$\frac{1}{8200}$	21.0 "		" "
. . .	22.5 "		alive
$\frac{1}{6400}$	26.5 "		"
. . .	22.5 "		"
$\frac{1}{12800}$	29.0 "		"

The results obtained from the three chlor-acetic acids are given in tables 49 to 51. At the concentration in which the lupines survive these acids are all practically completely dissociated. The mono- and di-chlor-acetic acids yield the critical concentration for hydrogen ions, namely, $\frac{1}{6400}$ gm. mol. per liter. Tri-chlor-acetic acid as well as mono-brom-acetic acid still kill the seedlings at this concentration. This fact shows that at least in the latter cases the anions have a distinct toxic effect of their own, which can of course be determined by investigation of the sodium salts of the acids in question. That amido-propionic acid (table 53) has no poisonous action at the concentration

tested is easily explained by the fact that the acid forms an inner salt and so does not yield hydrogen ions when dissolved in water.

49. MONO-CHLOR-ACETIC ACID.

(Begun January 20, 8 P.M.; closed January 21, 12 M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{3200}$	17.0 ^{mm}	flabby, dead
....	18.0 "	" "
$\frac{1}{6400}$	25.5 "	apparently normal
....	26.0 "	" "
$\frac{1}{12800}$	22.0 "	" "
....	24.5 "	" "

50. DI-CHLOR-ACETIC ACID.

(Begun January 20, 9 P.M.; closed January 21, 12 M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{3200}$	17.0 ^{mm}	flabby, dead
....	16.0 "	" "
$\frac{1}{6400}$	22.0 "	dead (?)
....	22.0 "	alive!
$\frac{1}{12800}$	24.0 "	apparently normal
....	25.0 "	" "

51. TRI-CHLOR-ACETIC ACID.

(Begun January 20, 9 P.M.; closed January 21, 12 M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{6400}$	18.5 ^{mm}	turgor gone, dead
....	19.0 "	" " "
$\frac{1}{12800}$	23.5 "	apparently normal
....	27.5 "	" "

52. MONO-BROM-ACETIC ACID.

(Begun January 20, 10 P.M.; closed January 21, 12:30 P.M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{6400}$	20.5 ^{mm}	turgor gone, dead
....	24.5 "	" " "
$\frac{1}{12800}$	28.5 "	turgid, living
....	24.0 "	" "

53. AMIDO-PROPIONIC ACID.

(Begun January 24, 8 P.M.; closed January 25, 3 P.M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{400}$	30.0 ^{mm}	alive
$\frac{1}{800}$	36.0 "	"
$\frac{1}{1600}$	33.0 "	"
.....	25.0 "	"

Eight dibasic acids of the fatty series were investigated. The results are given in tables 54 to 62. In the case of oxalic acid it will be noted that the concentration in which the seedlings survive is $\frac{1}{6400}$ gram equivalent per liter, the same, then, as in case of the strong mineral acids. Oxalic acid at this concentration is practically completely dissociated. Its toxic effect in this weak solution is due only to the hydrogen ions that the solution contains, for a gram-molecule of acid potassium oxalate has the same poisonous effect as half a gram-molecule of the acid (compare table 55).

54. OXALIC ACID.

(Begun January 14, 10 P.M.)

Concentration gm. equiv. per liter	Length Jan. 15, 10 A.M.	Length Jan. 15, 6 P.M.	Remarks
$\frac{1}{3200}$	19.0 ^{mm}	19.0 ^{mm}	dead
$\frac{1}{6400}$	24.0 "	27.0 "	alive
$\frac{1}{12800}$	25.5 "	30.0 "	"

55. ACID POTASSIUM OXALATE.

(Begun January 16, 5 P.M.; closed January 16, 6 P.M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{1600}$	17.0 ^{mm}	flabby, dead
.....	18.0 "	" "
$\frac{1}{3200}$	21.0 "	apparently alive (?)
.....	21.0 "	dead
$\frac{1}{6400}$	33.5 "	apparently normal
.....	26.5 "	" "

56. MALONIC ACID.

(Begun January 15, 6:30 P.M.; closed January 16, 3 P.M.)

Concentration gm. equiv. per liter	Length	Remarks
$\frac{1}{1600}$	18.0 ^{mm}	flabby, dead
$\frac{1}{3200}$	32.0 "	apparently normal
$\frac{1}{6400}$	29.0 "	" "

57. SUCCINNIC ACID.

(Begun January 15, 4 P.M.; closed January 16, 3 P.M.)

Concentration gm. equiv. per liter	Length	Remarks
$\frac{1}{800}$	17.5 ^{mm}	flabby, dead
. . .	16.0 "	" "
$\frac{1}{1600}$	25.0 "	alive
. . .	16.5 "	flabby, dead
$\frac{1}{3200}$	27.0 "	alive
. . .	33.5 "	"

58. FUMARIC ACID.

(Begun January 15, 5 P.M.; closed January 16, 3 P.M.)

Concentration gm. equiv. per liter	Length	Remarks
$\frac{1}{3200}$	20.5 ^{mm}	dead
$\frac{1}{6400}$	19.5 "	apparently living
. . .	28.0 "	apparently normal

59. MALEIC ACID.

(Begun January 15, 6 P.M.; closed January 16, 3 P.M.)

Concentration gm. equiv. per liter	Length	Remarks
$\frac{1}{1600}$	18.0 ^{mm}	dead
. . .	20.5 "	"
$\frac{1}{3200}$	29.0 "	living
. . .	23.5 "	"
$\frac{1}{6400}$	29.0 "	apparently normal
. . .	line gone	" "

Malonic acid (table 56) is dissociated to the extent of 82.3 per cent. when one gram equivalent is dissolved in 1024 liters, so that at the concentration one gram equivalent in 3200 (the concentration in which the lupines live) the acid is highly dissociated though probably not completely.

Succinnic acid is a much weaker acid. It is dissociated only 30.82 per cent. when one gram equivalent is contained in 1024 liters (Ostwald). Table 56 shows that some of the seedlings survive when one gram equivalent of the acid is contained in 1600 liters.

Fumaric acid (table 58) allows the beans to survive when one gram equivalent is contained in 6400 liters, whereas maleic acid (table 59) permits them to live when one gram equivalent is present in 3200 liters. As maleic acid at the dilution 1024 is dissociated²⁴ 98.2 per cent. and fumaric only 78.5 per cent., we should expect the latter to be less poisonous than the former, if the toxic action be due to the hydrogen ions alone. That the opposite apparently takes place seems to show that the anions of fumaric acid exert a toxic action at this high state of dilution. Whether this is true or not can only be definitely settled by investigating the action of a salt of the acid the cation of which has no toxic effect. We do not place much reliance on the results obtained from these two acids as it is questionable whether the substances were perfectly pure.

60. MALIC ACID.

(Begun January 28, 6 P.M.; closed January 29, 9 A.M.)

Concentration gm. equiv. per liter	Length	Remarks
$\frac{1}{1600}$	18.5 ^{mm}	flabby, dead
...	17.5 "	" "
$\frac{1}{3200}$	27.5 "	alive
...	20.5 "	"
$\frac{1}{6400}$	25.0 "	"

In a solution of malic acid (table 60) the seedlings survive when one gram equivalent is present in 3200 liters. This is about

²⁴ See Ostwald, Zeitschr. f. physik. Chem., 3: 380.

what one would expect considering the degree of the dissociation of this acid and the fact that at this concentration the hydrogen ions alone are active.

61. ASPARTIC ACID.

(Begun January 24, 9 P.M.; closed January 25, 4 P.M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{3200}$	18.5 ^{mm}	dead
....	16.5 "	"
$\frac{1}{6400}$	28.0 "	alive
....	31.0 "	"
$\frac{1}{12800}$	20.0 "	"
....	26.0 "	"

Aspartic acid (table 61) has a strong toxic action, the seedlings only surviving when the solution contains $\frac{1}{6400}$ gram-molecule per liter. The electrical conductivity of this acid is not given in Ostwald's tables. It is not probable that the acid is completely dissociated at this concentration, however. Whether the anion is active toxically can be determined by investigating the action of the sodium salt of the acid.

62. TARTARIC ACID.

(Begun January 15, 5 P.M.; closed January 16, 3 P.M.)

Concentration gm. equiv. per liter	Length	Remarks
$\frac{1}{3200}$	19.0 ^{mm}	dead
....	20.0 "	"
$\frac{1}{6400}$	29.0 "	alive
....	21.0 "	"

Tartaric acid (table 62) gives the limit $\frac{1}{6400}$ gram equivalent per liter. This acid is a relatively strong acid and is practically completely dissociated at this high dilution. We get only the effect of the hydrogen ions here, for a solution of sodium tartrate of like strength would not kill the seedlings.

Citric acid (table 63) was investigated in this connection. The critical limit, $\frac{1}{3200}$ gram equivalent per liter, found for this

acid is what one would have expected it to be from the concentration of the hydrogen ions in this solution.

63. CITRIC ACID.

(Begun January 24, 9 P.M.; closed January 25, 4 P.M.)

Concentration gm. equiv. per liter	Length	Remarks
$\frac{1}{1600}$	17.0 ^{mm}	dead
....	17.0 "	"
$\frac{1}{3200}$	20.0 "	living
....	20.0 "	"
$\frac{1}{6400}$	27.5 "	"
....	26.0 "	"
$\frac{1}{12800}$	28.5 "	"
....	26.0 "	"

The poisonous action of eleven acids of the aromatic series has been determined. The acids of this series are of special interest, for the undissociated molecules as well as the anions in nearly all cases possess a distinct toxic action of their own, even at great dilutions.

64. BENZOIC ACID.

(Begun January 14, 8 P.M.)

Concentration gm. mol. per liter	Length January 15, 9 A.M.	Length January 15, 6 P.M.	Remarks
$\frac{1}{3200}$	20.0 ^{mm}		dead
....	18.0 "		"
$\frac{1}{6400}$	22.5 "	24.0 ^{mm}	living
....	24.0 "	27.0 "	"
$\frac{1}{12800}$	26.5 "	29.0 "	"
....	23.0 "	25.0 "	"

65. HIPPURIC ACID.

(Begun January 23, 9 P.M.; closed January 24, 12 M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{3200}$	20.5 ^{mm}	dead
....	20.0 "	"
$\frac{1}{6400}$	26.5 "	alive
....	24.5 "	"
$\frac{1}{12800}$	28.5 "	"

Benzoic and hippuric acids (tables 64 and 65) are both relatively weakly dissociated, the former 21.61 per cent. and the latter 37.51 per cent. at the dilution 1024, according to Ostwald. Both of these acids kill the lupines until the concentration $\frac{1}{6400}$ gm. mol. per liter is reached. It is not probable that these weak acids are completely dissociated even at this great dilution. The result shows that here the toxic effect is due in a high degree to the undissociated molecules and the anions present. Whether the undissociated acid is more poisonous than the anions can be determined by testing the action of the sodium salts.

66. CINNAMIC ACID.

(Begun January 23, 9 P.M.; closed January 24, 12 M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{800}$	15.5 ^{mm}	turgor lost, dead
...	15.5 "	" " "
$\frac{1}{1600}$	16.0 "	" " "
...	16.5 "	" " "
$\frac{1}{3200}$	18.0 "	" " "
...	17.5 "	" " "
$\frac{1}{6400}$	23.5 "	" " "
...	20.5 "	" " "
$\frac{1}{12800}$	29.5 "	turgid, apparently normal
...	17.5 "	" " "

Cinnamic acid (table 65) is only dissociated to the extent of 17.34 per cent. at 1024, and yet in a solution of it the lupines will not survive until the acid is diluted so that it contains only $\frac{1}{12800}$ gm. mol. per liter. At this dilution we know that hydrogen ions are no longer harmful to the plants, hence the strong toxic action of this acid is due to the anions and the undissociated molecules present in the solution.

Another interesting group is that of the oxy-benzoic acids. The results obtained from the three monooxy-benzoic acids are given in tables 67 to 69. It will be seen that salicylic acid has the greatest poisonous action, the seedling surviving in a solution

that contains 1 gm. mol. in 6400 liters; then follows meta-oxy-benzoic acid, which is only fatal after the concentration 1 gm. mol. in 3200 liters is overstepped; and finally para-oxy-benzoic acid of which the radicles will bear 1 gm. mol. in 1600 liters.

67. SALICYLIC ACID.

(Begun January 14, 9 P.M.)

Concentration gm. mol. per liter	Length Jan. 15, 9 A.M.	Length Jan. 15, 6 P.M.	Remarks
$\frac{1}{3200}$	16.0 ^{mm}		dead
....	18.5 "		"
$\frac{1}{6400}$	24.5 "	26.0 ^{mm}	alive
....	18.5 "		dead
$\frac{1}{12800}$	26.0 "	29.0 "	alive

68. META-OXY-BENZOIC ACID.

(Begun January 23, 8 P.M.)

Concentration gm. mol. per liter	Length Jan. 24, 12 M.	Length Jan. 25, 3 P.M.	Remarks
$\frac{1}{1600}$	19.5 ^{mm}		flabby, dead
....	18.0 "		" "
$\frac{1}{3200}$	23.5 "	28.0 ^{mm}	living
....	23.5 "	28.5 "	"
$\frac{1}{6400}$	29.0 "		apparently n'r'ml
....	28.0 "		" "
$\frac{1}{12800}$	20.5 "		" "
....	24.5 "		" "

69. PARA-OXY-BENZOIC ACID.

(Begun January 23, 8 P.M.)

Concentration gm. mol. per liter	Length Jan. 24, 12 M.	Length Jan. 24, 7 P.M.	Remarks
$\frac{1}{1600}$	19.0 ^{mm}		flabby, dead
....	25.0 "	26.0 ^{mm}	living
$\frac{1}{3200}$	24.5 "	26.0 "	"
....	27.5 "	29.5 "	"
$\frac{1}{6400}$	32.5 "		apparently n'r'ml
....	32.0 "		" "
$\frac{1}{12800}$	25.5 "		" "
....	33.5 "		" "

The order of the poisonous action of these acids is, then, ortho, meta and para. This is also the order of their electrolytic dissociation, the degrees of dissociation of the three acids at the dilution 1024 being 62.80 per cent., 25.70 per cent. and 15.68 per cent. respectively, according to Ostwald. Whether the toxic action of these acids at the concentration at which they are fatal to the lupines is due in part to the anions here also calls for an investigation of the sodium salts.

As typical examples of other oxy-benzoic acids protocatechuic and gallic acids were chosen (see tables 70 and 71). The concentration of the former in which the beans survive is $\frac{1}{3200}$ gm. mol. per liter. The degree of dissociation of this acid at 1024 is 16.68 per cent., somewhat higher, then, than para-oxy-benzoic acid. Considering the action of the hydrogen ions alone, we should expect protocatechuic acid to be somewhat more poisonous than para-oxy-benzoic acid. It seems probable, however, that the action of the undissociated molecules and the anions can not be considered *nil* at the concentration 3200.

In the case of gallic acid, which is dissociated 18.72 per cent. at 1024, the seedlings survive only at the concentration 6400 as table 71 shows. Here clearly the anions and the undissociated molecules must have a toxic action of their own even at this high dilution, for the acid can clearly not be considered as completely dissociated.

70. PROTOCATECHUIC ACID.

(Begun January 24, 8 P.M.; closed January 25, 3 P.M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{1600}$	17.0 ^{mm}	flabby, dead
....	17.8 "	" "
$\frac{1}{3200}$	24.5 "	alive
....	18.5 "	dead
$\frac{1}{6400}$	27.0 "	alive
....	29.0 "	"
$\frac{1}{12800}$	29.0 "	"
....	28.0 "	"

71. GALLIC ACID.

(Begun January 23, 10 P.M.; closed January 24, 12 M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{1600}$	18.5 ^{mm}	dead
$\frac{1}{3200}$	24.0 "	"
$\frac{1}{6400}$	23.5 "	alive
$\frac{1}{12800}$	28.0 "	"

Finally the action of the three mono-nitro-benzoic acids was investigated. Tables 72 to 74 show that the ortho compound is least poisonous, seedlings surviving in the concentration 6400, whereas in both the meta and para compounds the solutions proved fatal until the concentration 12,800 was reached. The degrees of dissociation of these acids at 1024 are 87.9 per cent., 44.4 per cent. and 46.4 per cent. respectively. It is clear that in case of the meta and para acids, the toxic effect at 12,800 can no longer be due to hydrogen ions, and consequently must be ascribed to the undissociated molecules and the anions; as the concentration of the former is not great at this high dilution, it seems probable that the toxic action is mainly due to the anions. An investigation of the sodium salts will, of course, be necessary to decide this point definitely. Ortho-nitro-benzoic acid is practically completely dissociated at 6400. The anions of this acid are therefore less poisonous than hydrogen ions. The action of a solution of the sodium salt will very likely confirm this.

72. ORTHO-NITRO-BENZOIC ACID.

(Begun January 16, 5 P.M.; closed January 17, 12 M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{3200}$	19.0 ^{mm}	flabby, dead
....	18.5 "	" "
$\frac{1}{6400}$	36.0 "	apparently normal, living
....	29.0 "	" " "

73. META-NITRO-BENZOIC ACID.

(Begun January 16, 3 P.M.; closed January 17, 1 P.M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{6400}$	20.5 ^{mm}	dead
.....	16.0 "	"
$\frac{1}{12800}$	36.0 "	apparently normal
.....	36.0 "	" "

74. PARA-NITRO-BENZOIC ACID.

(Begun January 16, 6 P.M.; closed January 17, 12 M.)

Concentration gm. mol. per liter	Length	Remarks
$\frac{1}{8200}$	17.0 ^{mm}	flabby, dead
.....	17.0 "	" "
$\frac{1}{6400}$	21.0 "	dead
.....	19.0 "	"
$\frac{1}{12800}$	33.0 "	apparently normal
.....	33.0 "	" "

That the modern theory of solutions would throw light on their physiological action was to be expected. From the foregoing detailed results it is evident that in the case of plants the toxic action of solutions of electrolytes, when dissociation is practically complete, is due to the action of the ions present. When dissociation is not complete, the undissociated part of the electrolytes may also exert a toxic effect, as has been pointed out in several instances. We have here then, as it were, a recognition of the theory of electrolytic dissociation by the organic world.

Mr. F. D. Heald, Fellow in Botany at the University of Wisconsin, has investigated the action on other plants of a considerable number of the solutions which we have tested. The results that he obtained are presented in an accompanying paper. They are perfectly analogous to those that we have found, and hence strongly confirm our conclusions.

It is clear that a knowledge of the mere presence of a metal or other element in a solution does not allow one to draw a conclusion as to its physiological action; it must also be known as to whether that element exists as an ion by itself or is combined with other elements to form a complex ion. If the addition of certain substances to a solution containing a physiologically active ion forms a complex ion of much less powerful action, it follows that these additional ingredients afford a means of reducing, so to speak, the physiological action of the simple ion.

Although this work has thus far been carried out only with higher plants, investigations on bacteria that are being carried on in this connection at the Bacteriological Laboratory of the University of Wisconsin have already yielded results supporting the theory. Anyone inspecting Miquel's table of the efficiency of antiseptics in Sternberg's "*Manual of Bacteriology*," and at the same time bearing in mind the theory of Arrhenius, although the concentrations are given in per cent. instead of chemical equivalents, will be able to see in it, only in rough outline to be sure, the corroboration of the views here advanced. Experiments on animals are contemplated.

It will be seen that a wide field for research along physiological lines opens up by applying to the field of biology the dissociation theory that has proved so fertile in chemistry and physics. Further work in this direction, using the latest and best that the new physical chemistry has to offer, it is to be hoped will place our knowledge of the physiological action of solutions of electrolytes on a better basis than the purely empirical one on which it has thus far rested. It does not seem too much to expect that the effects of such study will soon be felt in agriculture and therapeutics, while bacteriological study pursued from the standpoint of the new theory will yield important additions to our knowledge of antiseptics.

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